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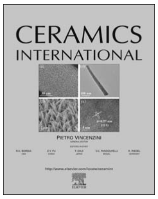

Properties and microstructure evolution of C_f/SiC composites fabricated by polymer impregnation and pyrolysis (PIP) with liquid polycarbosilane

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ABSTRACT

In the present study, a novel liquid polycarbosilane (LPCS) with a ceramic yield as high as 83% was applied to develop 3D needle-punched C_f/SiC composites via polymer impregnation and pyrolysis process (PIP). The cross-link and ceramization processes of LPCS were studied in detail by FT-IR and TG-DSC; a compact ceramic was obtained when LPCS was firstly cured at 120 °C before pyrolysis. It was found that the LPCS-C_f/SiC composites possessed a higher density (2.13 g/cm^3) than that of the PCS-C_f/SiC composites even though the PIP cycle for densification was obviously reduced, which means a higher densification efficiency. Logically, the LPCS-C_f/SiC composites exhibited superior mechanical properties. The shorter length and rougher surfaces of pulled-out fibers indicated the LPCS-C_f/SiC composites to possess a stronger bonding between matrix and PyC interphase compared with the PCS-C_f/SiC composites.

1. Introduction

Owing to the advantages such as lower density, better toughness and higher specific strength than monolithic silicon carbide (SiC) [1–3], continuous fiber reinforced SiC matrix composites have an increasingly extensive application prospect as high temperature structural components [4,5]. Researchers have been paying much attention to the fabrication of SiC-matrix composites in the past decades [6–8].

Currently, there are three mostly-applied methods for the fabrication of SiC-matrix composites, namely chemical vapor infiltration (CVI), liquid silicon infiltration (LSI) and polymer impregnation and pyrolysis (PIP) [9–11]. The CVI process can get near-stoichiometric SiC matrix but it's time-consuming and costly. In the LSI process, SiC matrix can be formed *in-stu* through the reaction between carbon and molten silicon. However, fiber damage caused by high temperature and reactive molten silicon as well as the existence of free silicon in matrix is the main concerns. Compared with them, the PIP process is a more promising method for the fabrication of SiC-matrix composites, due to its advantages in impregnation efficiency among fibers, microstructure control, large-scale components fabrication with complicated shapes and low cost [12,13].

Owing to the volume shrinkage and gas evaporation during the pyrolysis process of traditional solid-polycarbosilane (PCS), many PIP cycles are necessary to be repeated to get composites with an acceptable density, which leads to a lengthy fabrication route. Lots of efforts have been made to improve the densification efficiency of PIP process so far. Wang [14] investigated the microstructure evolution in the active filler enhanced PIP process, and found that most fillers preferred to remain in the intra-bundle areas, while almost no fillers were observed in the inter-bundle areas. The application of novel precursors is believed to be a promising solution to enhance the efficiency of PIP process. Kotani et al. [15] prepared SiC_f/SiC composites by the PIP process with the matrix precursor (PVS), a liquid precursor with a lot of functional Si-H bonds. High-performance composites were obtained via an effective cross-linking process. Luo et al. [16] fabricated SiC_f/SiC composites with the SiC precursor (LPVCS). It was illustrated that the density and densification efficiency of composites were improved remarkably. Yin et al. [17] revealed that the precursors would exert a significant effect on the densification process and mechanical properties of composites.

Allyhydridopolycarbosilane (AHPCS), which is partially allyl-substituted, was widely studied as SiC precursor for ceramic and composite

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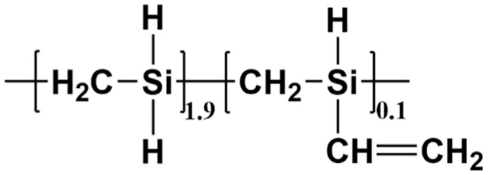

$$\left[H_2C-\underset{H}{\overset{H}{Si}}\right]_{1.9}\left[CH_2-\underset{CH=CH_2}{\overset{H}{Si}}\right]_{0.1}$$

Fig. 1. The scheme of the molecular structure of LPCS.

fabrication [18,19]. In this work, a commercial liquid polycarbosilane (LPCS, Chemistry Institute of Chinese Academy of Sciences), which is analogous to AHPCS but partially vinyl-subsituted, was introduced as the SiC precursor. Moreover, to enhance the densification process, low viscosity was realized by adjusting the molecular weight of LPCS. In order to keep low viscosity LPCS remaining in the preforms before converting to SiC matrix, low-temperature crosslinking of LPCS at 120 °C was performed with the assistance of Dicumyl peroxide (DCP). Furthermore, the effect of cross-linking process on the pyrolytic behavior of LPCS and the microstructure evolution of the C_f/SiC composites were studied. The densification efficiency of this novel PIP process was verified by comparison with the traditional PIP process. The differences in properties and microstructure evolution of the C_f/SiC composites prepared from different precursors were also investigated.

2. Experimental procedure

According to the manufacturer, the approximate formula of LPCS was $[CH_2SiH_{1.9}(CH{=}CH_2)_{0.1}]_n$ and the molecular structure of LPCS was depicted in Fig. 1. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the precursor is 1154 and 5723 respectively. The viscosity of LPCS at 25 °C ranges from 30 mPa s to 50 mPa s.

3D needle-punched preforms fabricated with T700 carbon fiber (12 K) were used as the reinforcements of the composites. Before the PIP process, pyrolytic carbon (PyC) interphase with a thickness of 300–350 nm was deposited on the preforms through chemical vapor infiltration at 1000 °C and 3 kPa using ethane as gas source.

The cross-linking process of LPCS was carried out at 120 °C for 8 h under the protection of Ar with 1 wt% DCP as crosslinking agent. The functional groups of LPCS before and after cross-linking process were analyzed by a FT-IR spectrometer (FTIR-7600, Lambda Scientific, Australia). Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of the cured LPCS were determined on a STA 409/PC simultaneous thermal analyzer (Netzsch, Germany) with a heating rate of 10 °C/min in flowing Ar.

During infiltration process, the preforms were placed in a container in vacuum, LPCS were injected into the container and then cured at 120 °C for 8 h. Subsequently, the composites were pyrolyzed at 1100 °C for 1 h with a heating rate of 5 °C/min in Ar atmosphere. The procedure of impregnation, curing and pyrolysis was repeated until the weight increase was less than 1%. For comparison, C_f/SiC composites fabricated using traditional solid-state PCS under the same conditions but with a high pressure for PCS solution infiltration were also given here. The densities as well as open porosities of the obtained composites were measured by Archimedes method.

The bending strength and elastic modulus of the final composites were characterized by three-point bending test (DDL20, Changchun Research Institute for Mechanical Science Co. Ltd, Changchun, China) with a span length of 50 mm and a crosshead speed of 0.5 mm/min respectively. The dimensions of the specimens for three-point bending test were 4 mm×6 mm ×60 mm. The fracture toughness was measured by a single edge notch beam (SENB) method, with the specimen size of 3 mm×6 mm ×30 mm, notch length of 3 mm, crosshead speed of 0.05 mm/min and a support span of 24 mm. For all the mechanical test in this work, at least five specimens were tested to give the mean value. Microstructures of composites were observed on both the fracture surfaces and polished cross-sections using a field-emission scanning electron microscope (Hitachi S-4800, Japan).

3. Results and discussion

3.1. Cross-link of LPCS

The optical photographs of LPCS with or without DCP cured at 120 °C are shown in Fig. 2. With the addition of 1 wt% DCP, liquid LPCS transforms into a solid after heat treatment at 120 °C for 8 h (Fig. 2(b)), while for the sample without DCP addition, it still keeps in a liquid state (Fig. 2(a)). After curing treatment, the weight loss of LPCS is less than 1%. It can also be observed that there are some cracks in the cured-LPCS, which may be caused by the density increase from 0.99 g/cm^3 to 1.06 g/cm^3 during the cross-linking process.

Fig. 3 compares the FT-IR spectrum of as-received LPCS with the spectrum of the cured one. Functional groups such as Si–CH_3, Si–CH_2–Si, Si–H, and –CH=CH_2 can be detected on the spectrum of the as-received LPCS. These groups can be identified as followed: bands at 3050 cm^{-1} and 3008 cm^{-1} representing C–H vibration in the CH=CH_2 and band at 1595 cm^{-1} assigned to C=C stretching of the Si-Vi, indicating the existence of Si-CH=CH_2; Si–H stretching at 2134 cm^{-1} and bending at 935 cm^{-1}; bands at 2960 cm^{-1} and 1404 cm^{-1} representing C-H stretching in Si–CH_3, and band at 1254 cm^{-1} assigned to Si–CH_3 stretching; bands at 1357 cm^{-1} and 1047 cm^{-1} indicating Si–CH_2–Si deformation and stretching respectively; wide bands from 843 cm^{-1} to 765 cm^{-1} ascribed to Si–C stretching [16,20–22]. After curing, significant differences in the FT-IR spectra can be observed. Firstly, the stretching band of C=C in –CH=CH_2 at 1595 cm^{-1} and

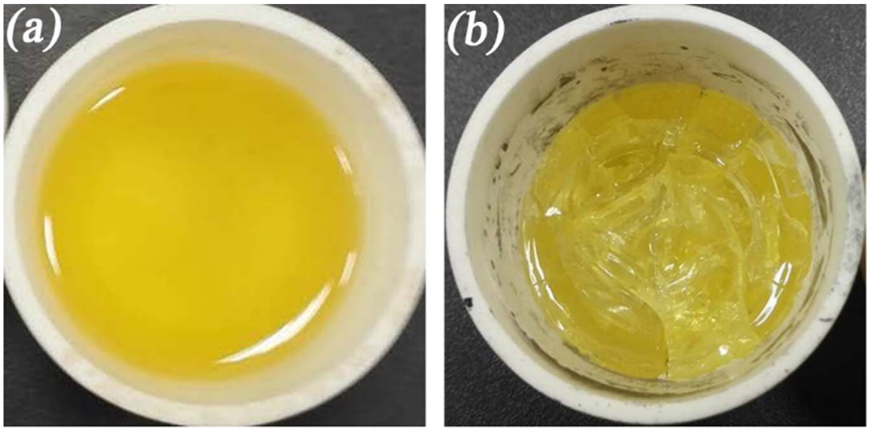

Fig. 2. Optical photographs of samples after heat-treatemt at 120 °C: (a) LPCS without 1 wt% DCP; (b) LPCS with 1 wt% DCP.